FE-P BEARING CALCAREOUS CONCRETIONS FROM ZIRC „MARBLE QUARRY" (TRANSDANUBIAN CENTRAL RANGE, HUNGARY)

by

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Abstract

Pelagic Tithonian limestone of 2 m thickness is paraconformably overlain by 0,5 m Barremian shallow marine limestone in the "Marble quarry" of Zirc. This single 2 – 3 m^2 Barremian limestone spot contains a rich, condensed Mediterranean ammonite fauna. Globular or half-cut concretions occur frequently on partly dissolved ammonite specimens, within the ammonite shells, and in the matrix. Two types were distinguished: the first is half-cut, cloudy, cauliflower-like one enclosed in the matrix, of 1 – 30 mm in diameter. The other type is globular or oval, of 10 – 20 mm in diameter. The structure is laminated, made of thin lamellae. The lamellae wedge out; frequent constrictions occur. Cores are built of tiny limestone fragments. Ca – P element composition was proved for the nodules by electron microprobe, surrounded by a Fe-rich crust. The latter contain clay minerals. Small amounts of adsorbed Mn and Ni occur on the surface of probably FeO(OH). X-ray investigations proved the Ca – P as apatite. The detailed textural, mineralogical and geochemical investigation of the nodules yielded more precise data on the ancient sedimentation environment. Probably the globular stromatolites, oncoids were formed above wave base, in a nearshore environment less than 50 m deep, where the formation of a continuous algal mat was not possible.

Introduction

The "Marble quarry" of Zirc is famous for its rich ammonite fauna, found by WEIN (1934), and investigated by NOSZKY (1934) and FÜLÖP (1964). NOSZKY determined the age of the fauna as Hauterivian, while he considered the Barremian age as an interval of bauxite formation. FÜLÖP (1964) has determined the megafauna more precisely and put the limestone of the "Marble quarry" into the Lower Barremian. Thus he denied the hypothesis of the Barremian continent, which lasted during the whole age.

This ammonitic limestone frequently contains layered concretions of brownish black colour. NOSZKY (1934) and FÜLÖP (1964) mentioned these as limonitic, clayey, manganese nodules.

Besides the determination and stratigraphic evaluation of the ammonite fauna we have to reconstruct the original environment of deposition. We have investigated the texture, mineralogy and geochemistry of the concretions from the "Marble quarry" to provide further data to the knowledge of this problem.

Most of the exposure in the "Marble quarry" of Zirc is made of a thick-bedded, light grey Tithonian limestone, paraconformably overlain by a

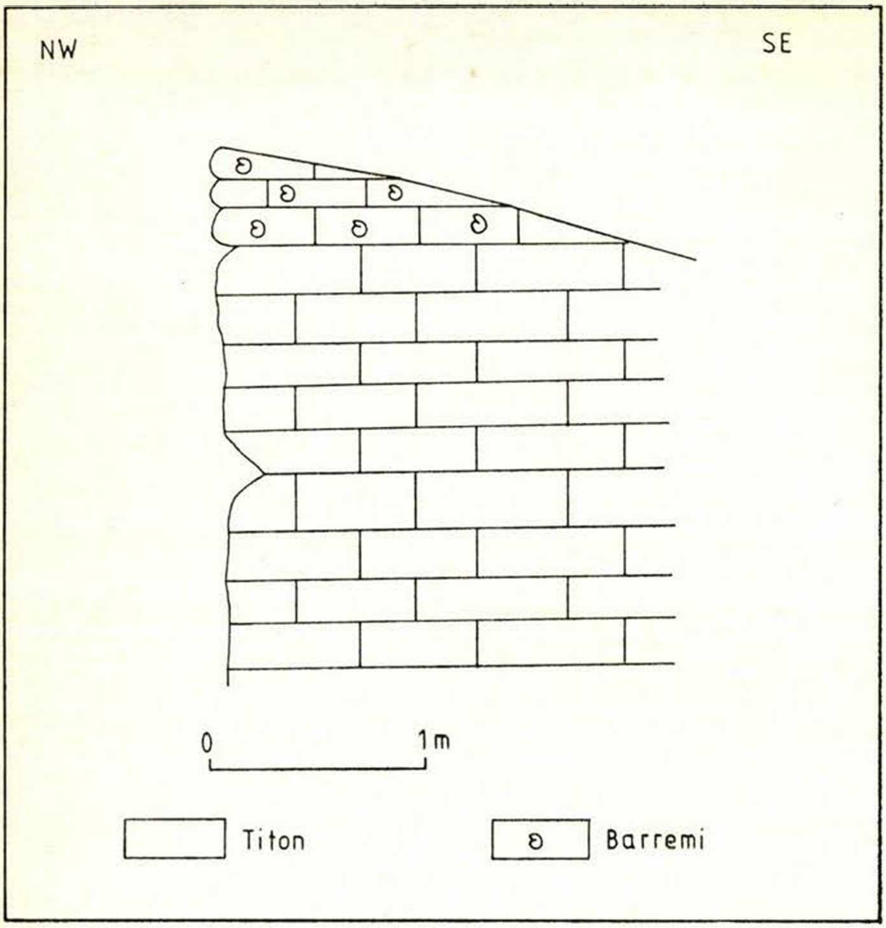


Fig. 1. The profile of „Marble quarry".

50 cm thick, compact, red to beige Barremian limestone bed. *(Fig. 1–2).*

The samples containing the concretions are from museum collections collected during 1940's and 50's by J. Fülöp.

Besides megascopic and microscopic textural and mineralogical investigations we have carried out X-ray and electron microprobe analyses. The latter were made by M. Polgári and J. Fórizs at the Geochemical Reserach Laboratory of the Hungarian Academy of Sciences on a Jeol/Superprobe 733.

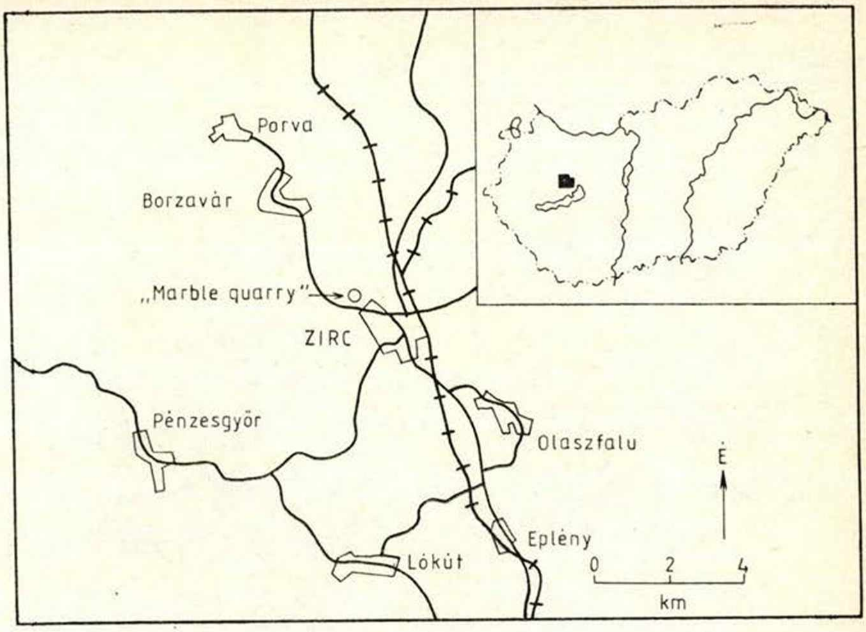


Fig. 2. Location chart of „Marble quarry".

Results

There are frequent cloudy, cauliflower-like and platy concretions on the resorbed surfaces of ammonites and in the limestone matrix. Their dimensions range from 1 – 2 mm to 2 – 3 cm. (Plate I). These are light brown coloured. Another group of the concretions are globular or oval with a diameter of 1 – 2 cm. Their colour is dark brown.

The structure of the concretions is laminated, formed of thin lamellae, looking like concentric at the first glance. Thin section investigations showed wedging out of lamellae and constrictions (Plate II, fig. 1 – 2).

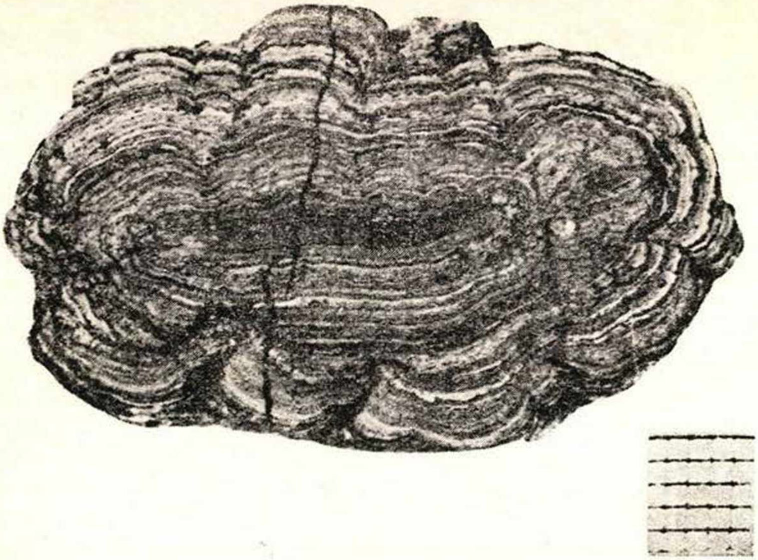
Cores of the concretions are formed of clastic grains, mostly of carbonate composition. The concretions frequently contain clastic mineral grains: quartz, rutile, ilmenite, magnetite, potash feldspar (plagioclase), mica (muscovite) and chlorite. The coloured components are mostly weathered, chloritised.

X-ray diffraction showed the concretions to be built of calcite (60 – 80%). Amount of quartz ranges from 5 to 10% and of apatite (phosphorite) from 0 to 20%.

Electron microprobe investigations were carried out on 9 concretions, covered by ca. 20 nm carbon film in a vacuum vaporizer to enhance electric conductivity. The results were surprising. The limonite-clay-manganese nodules described in the literature contain manganese in traces only. Consequently these cannot be considered as Mn-nodules. The dark laminae

PLATE I.

Concretions in limestone.



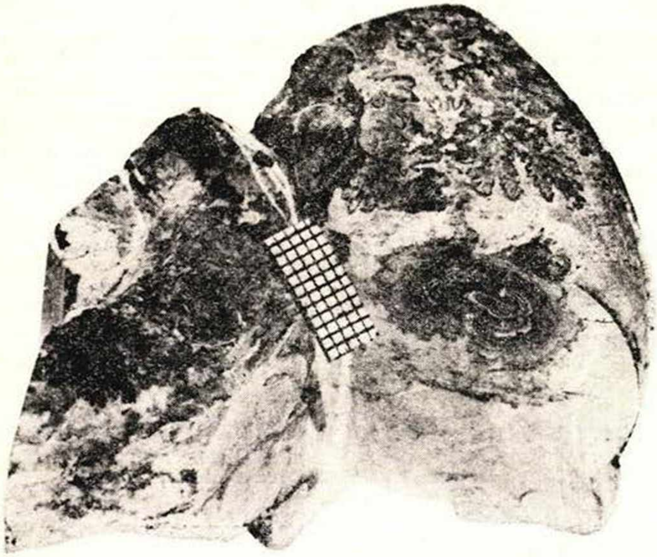


PLATE II.

Fig. 1. Macrooncoid with a limestone nucleus.
Fig. 2. Macrooncoid in an ammonite chamber.

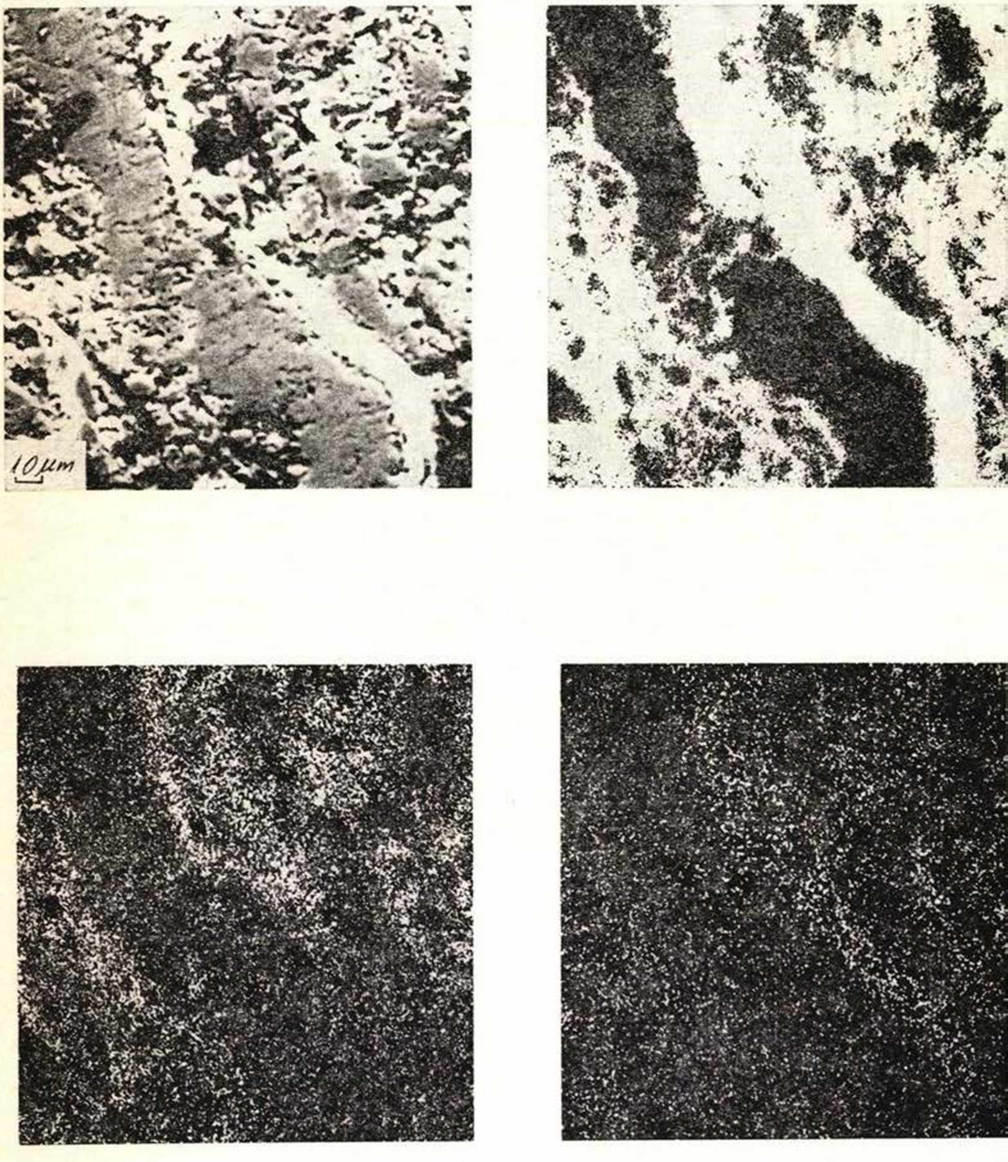

10 µm

PLATE III.

Fig. 1. Backscattered electron picture.
(The light parts are rich in Fe and contain small amount of Mn, Ni and clay, the grey phase is calcite.)
Fig. 2. X-ray area scan for Fe.
Fig. 3. X-ray area scan for Mn.
Fig. 4. X-ray area scan for Ni.

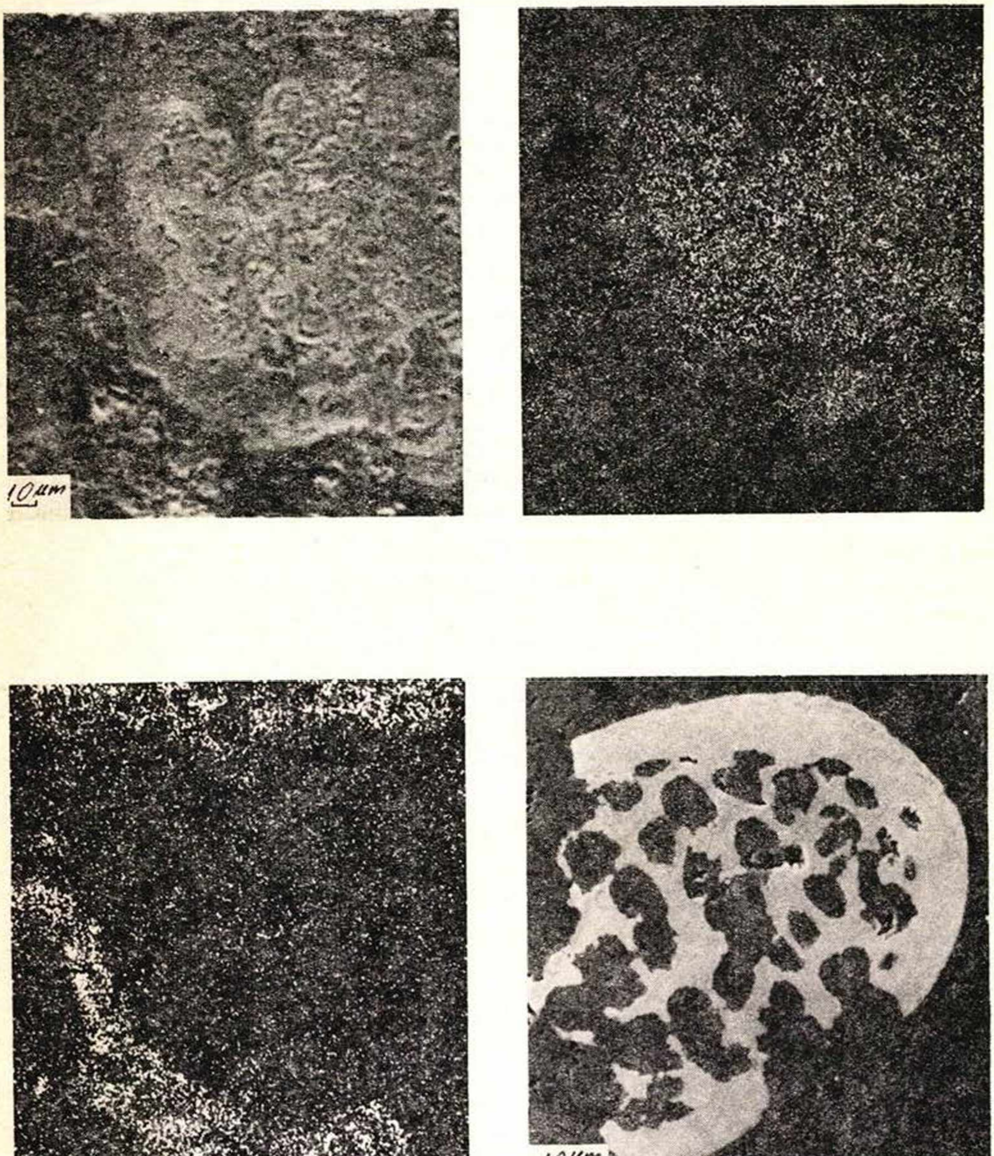

1,0µm
1,0µm

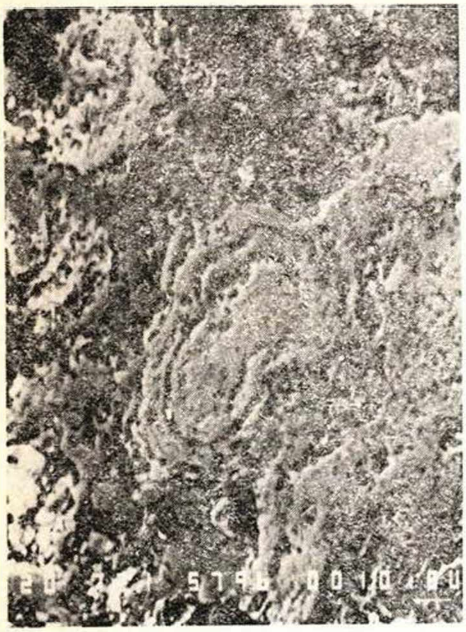
PLATE IV.

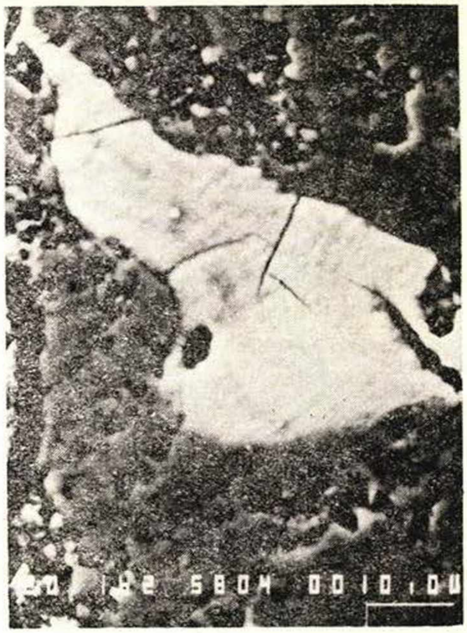
Fig. 1. Backscattered electron picture.
(The light-grey phase is/Ca, P), the dark-grey part is calcite, and the black crust around the phosphorite contains Fe- (Mn, Ti, Ni)-bearing clay.)

Fig. 2. X-ray area scan for P.

Fig. 3. X-ray area scan for Fe.

Fig. 4. Backscattered electron picture.
(The light phase is (Ca, P), the dark part is calcite).





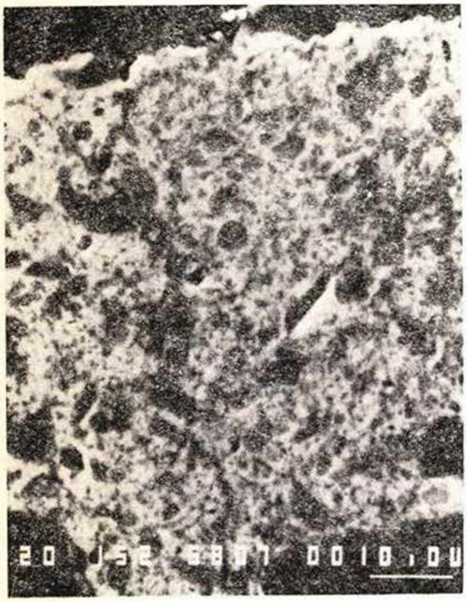


PLATE V.

Fig. 1. Backscattered electron picture.
(The light phase is (Ca, P)-concretion in limestone).

Fig. 2. Backscattered electron picture.
(The (Ca, P)-bearing phase (light phase) has sharp boundaries, and it has no any internal structure).

Fig. 3. Backscattered electron picture.
(The grain contains calcite (dark phase), and (Ca, P)-bearing phase (light part) in chaotic form).

Fig. 4. Backscattered electron picture.
(The limestone (dark parts) contains (Ca, P)-bearing phases of diffuse appereance.)

observed by the naked eye are rich in iron and show higher clay content. The Fe-rich phase locally contains trace amounts of Mn and Ni(Plate III). We could not decide, if the Fe-rich phase (goethite) or the clay adsorbed the Mn and Ni. Electron microprobe investigations did not allow more exact determination of the clay phase.

Both the concretions and the limestone matrix frequently contain Ca and P containing phases (phosphorite, apatite) of very variable appearance.

The limestone contains grains of Ca and P composition of probably biogenic origin (Plate IV), but also occur phases with sharp boundaries without any internal structure and phases of diffuse appearance. We have observed grains, which contain calcium carbonate and calcium phosphate in chaotic form (Plate V).

In the concretions there are Ca, P containing phases within the ferrous laminae, most probably of biogenic origin.

Phosphorite is frequent in the samples, reaching considerable amounts.

Discussion

It is very hard to differentiate between concretions and oncoids of algal origin and Fe-Mn nodules of chemical (bacterial) origin. Some types of the two nodules occur in similar sedimentary environments; their structure, size and element composition might be very similar. Their formation is the result of several factors (water depth, light, oxygen, Eh, pH, bacterial effects, currents, etc.).

The ferrous-carbonate concretions investigated by us barely contain manganese, consequently these cannot be considered as Mn-nodules. But ferrous concretions can be formed by purely chemical processes. The considerable Ca and P phase content of the carbonatic, ferrous concretions from the "Marble quarry" of Zirc, the structure of the phosphatic phase, the texture with laminae, wedging out of layers, and with constrictions (WENDT, 1970) provide evidence for the organic origin of the concretions.

Conclusions

If the algal origin of the Zirc concretions is true, it makes possible precise determination of the sedimentary environment (depth, currents, etc.), since algal activity can be observed in the upper 30–50 m depth of the sea. We think, that the ammonitic limestone of Zirc was deposited in a shallow marine environment of ca. 50 m depth. The algal nodules – concretions do not form a continuous algal mat; probably the environment was not suitable for the formation of it, due to the great depth or due to the effects of currents.

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